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FOR

A MEMBRANE/DISTILLATION METHOD AND SYSTEM FOR EXTRACTING CO_2 FROM HYDROCARBON GAS

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A MEMBRANE/DISTILLATION METHOD AND SYSTEM FOR EXTRACTING CO_2 FROM HYDROCARBON GAS

REFERENCE TO PENDING APPLICATIONS

This application is not based upon any pending domestic or international patent application.

REFERENCE TO MICROFICHE APPENDIX

This application is not referenced in any microfiche appendix.

FIELD OF THE INVENTION

The present invention relates to a method and system for treating a hydrocarbon mixture to remove CO_2 along with attendant sulfur compounds using distillation and membrane separation systems with critically arranged distillation reflux paths.

BACKGROUND OF THE INVENTION

Much of the world's natural gas supply is contaminated with unacceptably high levels of carbon dioxide (CO_2). In some cases, in addition to excessive CO_2, the natural gas may also contain excessive levels of sulfur compounds. Such sulfur compounds include hydrogen sulfide and carbonyl sulfide. In many cases, the carbon dioxide and sulfur contaminants lower the BTU value of natural gas making such gas unsuitable for use as a fuel or unsuitable to be transported in a pipeline carrier. Various commercial technologies including low temperature distillation, amine scrubbing and membrane separation, have been developed to upgrade natural gas containing excessive CO_2 or sulfur compounds. All of the above-mentioned technologies typically produce a useable natural gas stream and a carbon dioxide/sulfur compound stream. The distillation separation of CO_2 from hydrocarbon gas is a very energy and capital-intensive process. The present invention is an improvement on distillation technology that reduces the energy and capital requirement, producing a hydrocarbon product more efficiently.

Background information relating to the extraction of CO_2, with or without accompanying sulfur compounds, from hydrocarbon gas may be found in the following publications:

(1) *Process Can Efficiently Treat Gases Associated With CO_2 Miscible Flood* - Oil & Gas Journal, July 18, 1983.

(2) U.S. Patent No. 4,936,887 – Distillation Plus Membrane Processing of Gas Streams, Waldo et al., June 26, 1990.

(3) Canadian Patent No. 1,253,430 – Process and Apparatus for Fractionation of a Gaseous Mixture, Burr, May 2, 1989.

(4) U.S. Patent No. 4,417,449 – Process for Separating Carbon Dioxide and Acid Gases From a Carbonaceous Off-Gas, Hagarty et al., November 29, 1983.

(5) U.S. Patent No. 4,602,477 – Membrane-Aided Distillation for Carbon Dioxide and Hydrocarbon Separation, Lucadamo, July 29, 1986.

(6) U.S. Patent No. 4,444,571 – Energy Efficient Process for the Stripping of Gases from Liquids, Matson, April 24, 1984.

(7) U.S. Patent No. 4,374,657 – Process of Separating Acid Gases from Hydrocarbons, February 22, 1983.

SUMMARY OF THE INVENTION

The present invention relates to a membrane/distillation system for producing a CO_2 product, or a sour CO_2 product and a hydrocarbon product. The system is comprised of: (a) ancillary equipment for dehydrating, cooling, and temperature conditioning the inlet gas; (b) a distillation system for separating the conditioned inlet gas into a CO_2 liquid stream and a distillation overhead stream; (c) a primary condenser and reflux drum for separating the distillation overhead into a primary reflux stream and a hydrocarbon vapor stream, (d) a membrane system for separating the vapor stream into a hydrocarbon product and a permeate stream that is compressed, cooled and condensed to form additional reflux for the distillation column. The inlet hydrocarbon stream may be a natural gas stream or associated gas stream and may have liquid hydrocarbon components and which contains carbon dioxide and/or sulfur compounds. The hydrocarbon product may be a stream consisting predominantly of light hydrocarbons. The hydrocarbon product may include insignificant amounts of CO_2, sulfur containing species and other components. The CO_2 product may include insignificant amounts of hydrocarbon and other components, or the CO_2 product may be pure CO_2.

In one embodiment of the invention, the inlet gas stream is preconditioned for the separation by ancillary equipment. If required, inlet temperature, and pressure of the dehydrated hydrocarbon mixture are adjusted. After conditioning, the conditioned inlet stream is subjected to distillation. The distillation column produces an overhead stream and a CO_2 bottom product. The distillation overhead is further processed by a primary reflux system. The primary reflux system partially condenses the stream in a condenser. The partially condensed stream is separated by the primary reflux drum into a liquid reflux and hydrocarbon overhead. The liquid reflux is returned to the column. The hydrocarbon-enriched overhead vapor from the primary reflux drum is further separated by the membrane system. The membrane system separates the

reflux drum vapor into a hydrocarbon vapor stream and permeate stream. The permeate stream is compressed to a pressure greater than the distillation overhead. The compressed permeate stream is combined with the distillation overhead. This combined stream (distillation overhead and permeate stream) comprises the primary condenser inlet stream. This combined condenser inlet is fed to the primary reflux system which ultimately provides liquid reflux and membrane feed as described above.

In a separate embodiment of the invention, the inlet hydrocarbon fluid mixture is initially preconditioned and separated by the distillation system. If required, the inlet temperature and pressure of the dehydrated hydrocarbon mixture are adjusted. After conditioning, the inlet stream is subjected to fractional distillation. The distillation column produces an overhead stream and a CO_2 bottom product. The distillation overhead is further processed by a primary reflux system. The primary reflux system partially condenses the condenser inlet stream in the primary condenser. The partially condensed stream is separated by the primary reflux drum into a liquid reflux and hydrocarbon overhead. The overhead hydrocarbon vapor from the primary reflux drum provides a partial feed to the membrane system. The membrane system separates the membrane inlet stream into a hydrocarbon product and a permeate stream. The permeate stream is compressed to a pressure greater than the primary reflux. The permeate stream is partially condensed in a secondary condenser and a secondary reflux drum is used to separate the two phase fluid. The pressurized liquid from the secondary reflux drum is added to the primary reflux downstream of the primary condenser. The hydrocarbon vapor from the secondary reflux drum is combined with the hydrocarbon vapor stream from the primary reflux drum. This combined stream comprises the membrane inlet stream.

In either of the above embodiments of the invention, the CO_2 bottom product from the

fractional distillation is processed identically. The stream is partially vaporized in a reboiler heater. A reboiler separator produces a vapor for re-introduction into the column and a CO_2 liquid product. A portion of the CO_2 liquid product may optionally be used to satisfy the cooling requirements of the process. In this mode of operation, a CO_2 gas product is also produced.

The conditioned inlet gas required as feed to this invention may be obtained by a variety of methods well-known to those skilled in the art. The dehydrating system may be a glycol absorption system, a desiccant absorption system or a membrane dehydration system. For purposes of this invention, a dehydrating system is defined as a system that removes water from the stream to a dew point of less than the lowest temperature observed in the system.

A cooling system for the purposes of this invention may be a heat exchange system, a gas expansion system, a turbo expander system, a valve expansion system, or a mechanical refrigeration system. The heat exchange system is defined as one or more heat exchangers which utilize ambient temperature, or temperature of internal process streams, to decrease the temperature of the specified stream. A heat exchange system may consist of aerial-type exchangers, shell and tube, or plate and frame-type exchangers, which transfer heat from one process stream to another. An expansion system, either gas or liquid, is the expansion of a process stream to a condition of lower pressure. A turbo expander system is the expansion of this process stream through a turbo expander. In a turbo expander system, the expansion or pressure reduction of the gas stream is used to generate mechanical energy and effect a cooling of the process stream. A valve expansion system is the expansion or pressure reduction of this process stream through a valve or an orifice. The pressure reduction causes the gas stream to cool. A mechanical refrigeration system is the reduction of a process temperature by use of cooling derived from a refrigeration source that is ancillary to the process streams. In a

mechanical refrigeration system, a refrigerant is contained in a closed loop. The refrigerant is subjected to pressurization, expansion and condensation. On expansion, the pressurized refrigerant vaporizes and cools. This cooling is utilized in a cross exchanger to reduce the temperature of the process stream. The heat loss from the cross exchange causes condensation of the refrigerant stream. The condensed refrigerant is again pressurized and the cycle repeated.

A preferred temperature range of the cooling procedure of step (a) is from about –30°F to about 150°F and more preferably between –20°F and 60°F.

The system of the present invention may comprise a depressurizing device for optimizing the properties of inlet streams for separation by components of this invention. Distillation and membrane separation are the primary components. Typical depressurizing devices are a compressor, a turbo expander, and an expansion valve. The separation system of the present invention may also comprise a pump and a compressor. The pressure of the pressuring adjusting step (b) is from about 200 psia to about 1200 psia, and preferably from 350 psia to 800 psia and most preferably between 550 and 650 psia.

The distillation system is defined as a separation device that utilizes differences in boiling point and relative volatility to effect separation of components. The distillation system may have a plurality of distillation columns and the columns may be in a series or recycle configuration. Typical distillation columns employ trays and weirs to effect the successive steps of rectification and equilibration required for distillation. The column has a reflux produced by an overhead reflux system (condenser and separator drum) and reboiler vapor produced by a bottom fluid boiler and separator drum.

The membrane system is defined as a system which utilizes a selective barrier that is capable of separating components on the basis of size, shape or solubility. The membrane

system separates a high-pressure feed stream into a high-pressure non-permeate stream and a lower pressure permeate stream. Membranes that preferentially permeate CO_2 faster than hydrocarbons are useful for this invention. Membranes of this type are typically comprised of a glassy polymer. A glassy polymer is a polymer that is applied at a temperature lower than the glass transition. Examples of polymer families that are typically employed as glassy polymer membranes include: cellulose acetate, polyaramides, polybenzoxazoles, polycarbonates, polyimides, and polysulfones. Structural modification of the base polymer backbone is often used to enhance the gas separation performance of a given polymer family. These structural variants are also useful in this invention.

The membrane system has at least one membrane unit. The membrane system can have a plurality of membrane units. Often, the plurality of membrane units are arranged in a series configuration. The series configuration leads to improved performance when the membrane module performance is less than predictions based on an ideal membrane unit. A recycle configuration of the membrane modules can also be used to reduce hydrocarbon losses.

In one embodiment, the process comprises the step of recovering energy from the stream of CO_2 liquid from the bottom of the distillation column. By flashing all or a part of the liquid across an expansion valve, sufficient refrigeration can be achieved to meet or exceed the cooling requirements of the system. Furthermore, this mode of operation eliminates the necessity of ancillary mechanical refrigeration.

In another embodiment, the present invention relates to a process for producing high levels of CO_2 liquid and a hydrocarbon product. The process comprises the steps of: (a) cooling dehydrated hydrocarbon fluid mixture; (b) adjusting the pressure of the hydrocarbon fluid mixture; (c) distilling the hydrocarbon fluid mixture to produce a CO_2 liquid and a hydrocarbon

byproduct containing CO_2 and/or sour gas; and (d) utilizing a membrane system to further separate the hydrocarbon byproduct to produce a recoverable hydrocarbon product and an additive for distillation column reflux. In this embodiment, mechanical refrigeration is used for the cooling step (c) and, the CO_2 liquid from the bottom of the distillation column (c) is collected as product.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 represents a schematic flow diagram of a preferred embodiment of the present invention.

FIG. 2 represents a schematic flow diagram of the system of the present invention wherein a permeate stream from a membrane system is condensed in a separate condenser and added to the vapor from the distillation column condenser to provide feed for the membrane system.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Major elements of the invention are indicated in the drawings by numerals as follows:

14	Inlet gas stream
16	Inlet cross heat exchanger
18	Cooled inlet stream
20	Reboiler cross heater
22	Conditioned inlet stream
24	Distillation column
26	CO_2 bottom product stream
28	Distillation overhead stream
30	Permeate stream
32	Combined condenser inlet stream
34	Primary condenser
36	Primary condenser outlet stream
38	Primary reflux drum
40	Hydrocarbon vapor stream
42	Primary reflux liquid stream
44	Primary reflux pump
46	Pumped primary reflux liquid stream
48	Membrane unit
49	Membrane inlet
50	Permeate cross heat exchanger
52	Hydrocarbon gas product stream
54	Permeate stream
56	Compressor
58	Compressed permeate stream
60	First permeate cross heat exchanger feed stream
62	Second permeate cross heat exchanger feed stream
64	Permeate cross heat exchanger outlet stream

66	Hydrocarbon product cross heat exchanger
68	Hydrocarbon product cross heat exchanger outlet stream
70	CO_2 bottom product pump
72	Pumped CO_2 bottom product stream
74	Reboil/separator
76	Reboiler separator inlet stream
78	Reboiler separation vapor stream
80	Reboiler separation liquid stream
82	Primary CO_2 refrigerant stream
84	CO_2 liquid product
86	Primary refrigerant pressure reduction device
88	Primary condenser refrigerant inlet stream
90	Primary condenser refrigerant outlet stream
92	CO_2 gas product
94	Hydrocarbon gas product
96	Secondary reflux drum
98	Secondary condenser
102	Secondary condenser outlet stream
104	Secondary reflux liquid stream
106	Combined reflux liquid stream
108	Secondary CO_2 refrigerant stream
110	Secondary refrigerant pressure reduction device
112	Secondary condenser refrigerant inlet stream
114	Secondary condenser refrigerant outlet stream
116	Combined refrigerant outlet stream
118	Secondary hydrocarbon vapor stream

Referring now to the drawings wherein like reference numerals designate identical or corresponding parts throughout the several views and more particularly to FIG. 1 wherein the system and method of the present invention are illustrated. A dehydrated hydrocarbon fluid

mixture gas stream inlet which contains high levels of carbon dioxide flows by way of inlet gas stream **14** and enters an inlet cross heat exchanger **16** for conditioning. The resulting cooled inlet stream **18** enters a reboiler cross heater **20** for further conditioning, producing a conditioned inlet stream **22**. Stream **22** may be further cooled using a chiller. If the pressure of conditioned inlet stream **22** exceeds the critical pressure, either a Joule-Thomson expander or a turbo-expander can be used to reduce the pressure of conditioned inlet stream **22**. The energy from the expander can be used for compression or for generating electricity.

Upon completion of the cooling process and pressure reduction processes, the hydrocarbon fluid mixture gas stream is properly conditioned for distillation separation. A distillation separation system that produces a high yield of liquid CO_2 is preferred. The primary reason for selecting distillation for the bulk removal of CO_2 is its ability to remove the CO_2 as a liquid. Conditioned inlet stream **22** is distilled in distillation column **24** producing a liquefied CO_2 bottom product stream **26** and a distillation overhead stream **28** (containing significant amounts of CO_2). The distillation overhead stream **28** is combined with permeate stream **30** from the membrane unit **48** producing combined condenser inlet stream **32**. This stream **32** is cooled by primary condenser **34** producing a primary condenser outlet stream **36**. This stream **36** enters a primary reflux drum **38** producing a hydrocarbon vapor stream **40** and a primary reflux liquid stream **42**. This liquid stream **42** flows back to distillation column **24** by gravity or is pumped by primary reflux pump **44** to enter a top tray of distillation column **24** as reflux. The hydrocarbon vapor stream **40** is sent to membrane unit **48** for further CO_2 removal. Hydrocarbon vapor stream **40** enters permeate cross heat exchange **50** and is warmed prior to entering membrane unit **48**. The membrane unit may be a single stage or multiple stages depending on the application, in addition, the permeate pressure of the membrane stages can be different to

optimize compressing the permeate gas. Membrane separation produces a hydrocarbon product stream **52** and permeate stream **54**. For this example, permeate stream **54** is compressed in a compressor **56** producing a compressed permeate stream **58**. This stream **58** is divided into first and second permeate cross heat exchanger feed streams **60** and **62.** These streams are cooled by permeate cross heat exchanger **50** and hydrocarbon product cross heat exchanger **66** producing permeate cross heat exchanger outlet stream **64** and hydrocarbon product cross heat exchanger outlet stream **68** that combine to form permeate stream **30**.

Permeate stream **30** is then combined with distillation overhead stream **28** from the distillation column overhead to form combined condenser inlet stream **32**. Permeate stream **54** could also be removed for disposal or for further processing instead of being utilized for reflux enhancement.

The CO_2 bottom product stream **26** may be pumped to an elevated pressure using pump **70** into stream **72**. Thermal energy from the pumped CO_2 bottom product stream **72** is then recovered using reboiler cross heater **20** to cool inlet stream **18**. The reboiler separator inlet stream **76** enters a reboiler/separator **74**. The vapor from reboiler/separator **74**, stream **78,** is returned to the bottom of distillation column **24**. The liquid from reboiler/separator **74**, stream **80,** is split into a primary CO_2 refrigerant stream **82** for chilling, with the balance, stream **84** remaining as a CO_2 liquid product stream. Primary CO_2 refrigerant stream **82** is reduced in pressure with a primary refrigerant pressure reduction device **86** producing primary condensed refrigerant inlet stream **88**. This stream **88** enters primary condenser **34** providing cooling sufficient to produce the required reflux liquid stream **42.** Primary condenser refrigerant outlet stream **90** leaving primary condenser **34** enters inlet cross heat exhange **16** as an economizer to cool the inlet gas. The CO_2 gas stream leaving inlet cross heat exchange **16** as a gas stream **92**

can be compressed to combine with liquid CO_2 product stream **84** or can be used as a CO_2 gas product stream.

For a typical application with an inlet gas of 58% CO_2 at 610 psia, the process, as shown in FIG. 1, produces a hydrocarbon product containing 10% CO_2 at 565 psia and recovers 89.9% of the hydrocarbon in the inlet gas stream. The CO_2 gas product stream contains 92.8% CO_2 and recovers 89.1% of the CO_2 at 200 psia. The CO_2 liquid product stream contains 92.8% CO_2 and recovers 3.7% of the CO_2 at 610 psia. This gives a total recovery of CO_2 for this example of 92.8%. A significant demand for energy in any CO_2 removal process producing gaseous CO_2 is compression of the CO_2. CO_2 compression can be the limiting factor for projects requiring CO_2 at elevated pressures such as enhanced oil recovery, or re-injection of the CO_2 to eliminate venting to the atmosphere. The compression requirements for this process are less than that for traditional distillation processes, since the CO_2 product streams are produced at a relatively high pressure, and no external refrigeration is required.

Referring now to **FIG. 2**, wherein like reference numerals designate identical or corresponding parts, a dehydrated hydrocarbon fluid mixture inlet gas stream **14** that contains carbon dioxide enters inlet cross heat exchanger **16** for cooling. The resulting cooled inlet stream **18** enters a reboiler cross heater **20** for further cooling, producing conditioned inlet stream **22** which may be further cooled using a chiller. If the pressure of conditioned inlet stream **22** exceeds the critical pressure, either a Joule-Thomson expander or a turbo expander can be used to reduce the pressure thereof. Energy from an expander can be used for compression of the permeate gas or for generating electricity.

Upon completion of the cooling process and pressure reduction process, the hydrocarbon fluid mixture is properly conditioned for distillation separation. A distillation separation system

that produces a high yield of liquid CO_2 is preferred. The primary reason for selecting distillation for the bulk removal of CO_2 is its ability to remove the CO_2 as a liquid. Conditioned inlet stream **22** is then distilled in distillation column **24** producing a CO_2 bottom product stream **26** and a distillation overhead stream **28**, which contains significant amounts of CO_2. The distillation overhead stream **28** is cooled by primary condenser **34** producing primary condenser outlet stream **36** that enters primary reflux drum **38** producing a hydrocarbon vapor stream **40** and a primary reflux liquid stream **42**. This primary reflux liquid stream **42** is combined with secondary reflux liquid stream **104** from the secondary reflux drum **96**.. The combined reflux liquid stream **106** flows to a top tray of distillation column **24** as a reflux.

Hydrocarbon vapor stream **40** from primary reflux drum **38** is combined with secondary hydrocarbon vapor stream **118** and enters permeate cross heat exchanger **50** and is warmed prior to entering membrane unit **48**. The membrane unit **48** may be single stage or multiple stages depending on the application. In addition, the permeate pressure of the membrane stages can be different to optimize compressing the permeate gas. Separation in membrane unit **48** produces a hydrocarbon product stream **52** and a permeate stream **54**. Stream **54** is then compressed in compressor **56** producing compressed permeate stream **58** that is cooled by heat exchangers **50** and **66** producing permeate stream **30**. The permeate stream **30** is then partially condensed using secondary condenser **98** producing secondary condenser outlet stream **102**. Secondary reflux drum **96** produces secondary hydrocarbon vapor stream **118** and secondary reflux liquid stream **104**. Vapor stream **118** is combined with vapor stream **40** from primary reflux drum **38**. The combined stream is feed to membrane unit **48**. Secondary reflux liquid stream **104** is combined with pumped primary reflux liquid stream from primary reflux drum **38** to provide the combined reflux liquid stream **106** that feeds onto an upper tray in distillation column **24**.

The liquefied CO_2 bottom product stream **26** may be pumped to an elevated pressure using pump **70**. Thermal energy from the pumped bottom product stream **72** is then recovered using heat exchanger **20** to cool inlet stream **18**. The high concentration reboiler separator inlet stream **76** leaving heat exchanger **20** enters reboiler/separator **74**. The vapor from reboiler/separator **74**, stream **78** is returned to the bottom of distillation column **24**. Liquid from reboiled/separator **74** is split into secondary CO_2 refrigerant stream **108** and reboiler separation liquid stream **80.** Stream **108** is reduced in pressure with a secondary refrigerant pressure reduction device **110** providing secondary condenser refrigerant stream **112** that enters secondary condenser **98** providing cooling sufficient to produce the required reflux stream **104** that is fed to distillation column **24**. The secondary refrigerant outlet stream **114** leaving secondary condenser **98** is combined with primary refrigerant outlet stream **90** and enters inlet cross heat exchange **16** as an economizer to cool the inlet gas to the process. CO_2 gas leaving heat exchange **16** as product **92** can be compressed to combine with liquid CO_2 stream **84** or retained as a CO_2 gas product stream.

For a typical application with an inlet gas of 58% CO_2 at 610 psia, the process as shown in the drawing produces a hydrocarbon gas product containing 10% CO_2 at 565 psia and recovers 91% of the methane in the inlet. The CO_2 product gas stream contains 92.8% CO_2 and recovers 88.2% of the CO_2 at 200 psia. The CO_2 liquid product stream contains 92.8% CO_2 and recovers 4.6% of the CO_2 at 610 psia. This gives a total recovery of CO_2 for this example of 92.8%. A significant demand for energy in any CO_2 removal process producing gaseous CO_2 is compression of the CO_2. CO_2 compression can be the limiting factor for projects requiring the CO_2 at elevated pressure such as enhanced oil recovery, or re-injection of the CO_2 to eliminate venting to the atmosphere. The compression requirements for this process are less than that for a

traditional distillation process since the CO_2 product streams are produced at a relatively high pressure and no external refrigeration is required.

While the invention has been described with a certain degree of particularity, it is manifest that many changes may be made in the details of construction and the arrangement of components of the equipment and systems used in the invention, as well as the steps and sequence thereof, of practicing the methods of the invention without departing from the spirit and scope of this disclosure. It is understood that the invention is not limited to the embodiments set forth herein for purposes of exemplification, but is to be limited only by the scope of the attached claim or claims, including the full range of equivalency to which each element or step thereof is entitled.